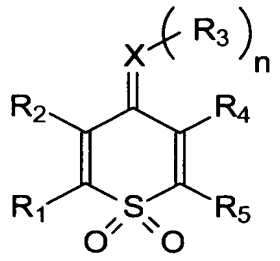
CLAIMS:

1. An electrochromic material comprising a substituted-1,1-dioxo-thiopyran of the general structure I:



I

wherein:

X is carbon, nitrogen, oxygen, or sulfur;

n is 0, 1 or 2;

R3 is independently an electron withdrawing group or a substituted or unsubstituted alky or aryl group;

R1 and R5 each independently represent a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group; and

R2 and R4 each independently represent hydrogen, or an electron withdrawing group, or a substituted or unsubstituted alkyl group.

2. The electrochromic material of claim 1 wherein R3 represents an electron withdrawing group selected from the group consisting of halogen, cyano, COOH, CO_2CH_3, CO_2-alky, $CON(C_2H_5)_2$, SO_2CH_3, SO_2-aryl SO_2CF_3, SO_2-alkyl, PO_3H_2, SO_3H, $B(OH)_2$, or $SO_2N(C_2H_5)_2$].

3. The electrochromic material of claim 1 wherein, when n > 0, R3 represents separately or independently substituted or unsubstituted aryl or substituted or unsubstituted alkyl.

4. The electrochromic material of claim 1 wherein said substituted or unsubstituted aryl group is phenyl or naphthyl.

5. The electrochromic material of claim 1 wherein said substituted or unsubstituted heterocyclic group is pyridine, pyrolle, furan, or thienyl.

6. The electrochromic material of claim 1 wherein R1 and R2 or R4 and R5, together with the carbon atoms to which they are attached, form a fused saturated or unsaturated 5- or 6- membered ring.

7. The electrochromic material of claim 1 wherein R2 and R4 each independently represent a hydrogen.

8. The electrochromic material of claim 1 wherein R2 and R4 each independently represent an electron withdrawing group selected from the group consisting of halogen, cyano, COOH, CO_2CH_3, CO_2-alky, $CON(C_2H_5)_2$, SO_2CH_3, SO_2-aryl SO_2CF_3, PO_3H_2, SO_3H, $B(OH)_2$, $SO_2N(C_2H_5)_2$] or a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group.

9. The electrochromic material of claim 1 wherein X represents carbon and the value of n is 2.

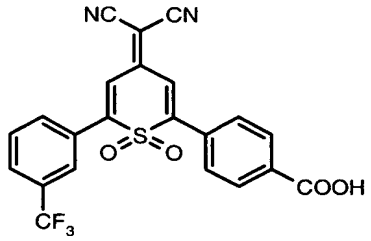
10. The electrochromic material of claim 9 where R3 is halogen, cyano, COOH, CO_2CH_3, CO_2-alky, $CON(C_2H_5)_2$, SO_2CH_3, SO_2-aryl SO_2CF_3, PO_3H_2, SO_3H, $B(OH)_2$, $SO_2N(C_2H_5)_2$].

11. The electrochromic material of claim 9 where R3 is a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group.

12. The electrochromic material of claim 9 where R3 together with the carbon atoms to which they are attached may form a fused saturated or unsaturated 5 or 6-membered ring containing one or more electron withdrawing groups.

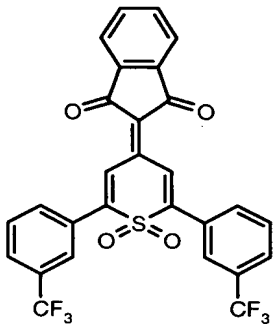
13. The electrochromic material of claim 9 wherein R3 is cyano, alkyester, or indanone.

14. The electrochromic material of claim 9 wherein said electrochromic material is represented by the following structure:



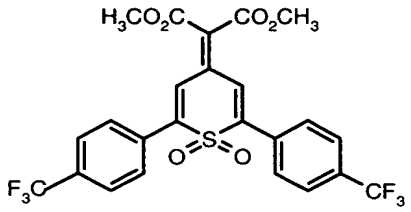
I-7.

15. The electrochromic material of claim 9 wherein said electrochromic material is represented by the following structure:



I-33.

16. The electrochromic material of claim 9 wherein said electrochromic material is represented by the following structure:

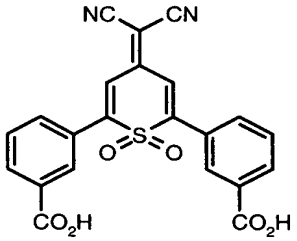


I-44.

17. The electrochromic material of claim 9 that incorporate that incorporate functional groups that facilitate the irreversible chemisorption nanocrystalline metal oxide electrodes.

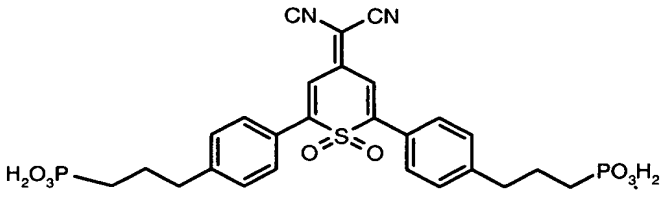
18. The electrochromic material of claim 9 wherein R1 thru R5 together or separately comprise carboxylate, salicylate, or phosphonate groups that facilitate irreversible chemisorption towards metal oxide electrodes.

19. The electrochromic material of claim 9 wherein the electrochromic material is represented by the following structure:



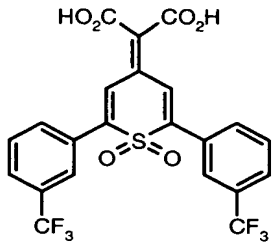
I-14.

20. The electrochromic material of claim 9 wherein the electrochromic material is represented by the following structure:



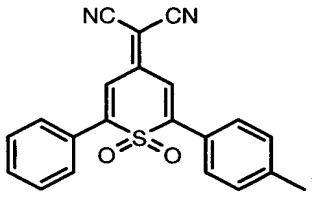
I-67.

21. The electrochromic material of claim 9 wherein the electrochromic material is represented by the following structure:



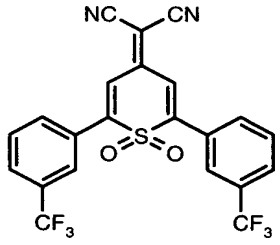
I-46.

22. The electrochromic material of claim 9 wherein said electrochromic material is represented by the formula:



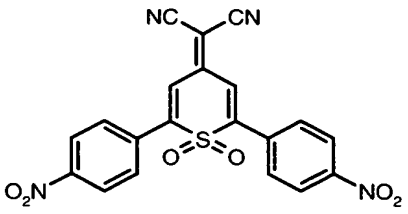
I-2.

23. The electrochromic material of claim 9 wherein said electrochromic material is represented by the formula:



I-6.

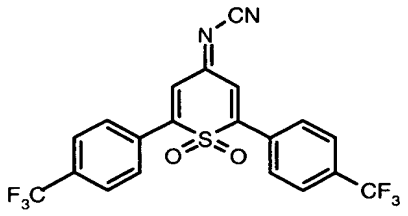
24. The electrochromic material of claim 9 wherein said electrochromic material is represented by the formula:



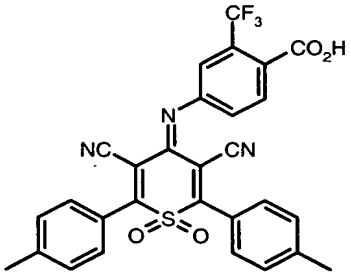
I-8.

25. The electrochromic material of claim 1 wherein X represents nitrogen and n is 1.

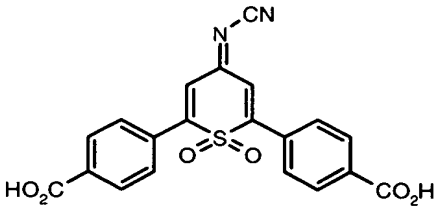
26. The electrochromic material of claim 25 wherein said electrochromic material is at least one member selected from the group consisting of:



I-50,



I-71, or



27. The electrochromic material of claim 1 wherein X is oxygen or sulfur, and the value of n is 0.

28. The electrochromic material of claim 1 wherein said electrochromic material has an electrochemical reduction potential of from –1.0 to +0.2 Volts vs SCE.

29. The electrochromic material of claim 1 wherein said electrochromic material has an electrochemical reduction potential of from –0.8 to –0.1 Volts vs SCE..

30. The electrochromic material of claim 1 wherein said electrochromic material has an electrochemical reduction potential of from –0.6 to –0.2 Volts vs SCE.

31. The electrochromic material of claim 1 wherein said electrochromic material comprises electrochromic sulfone structures that have groups for linking to nanocrystalline TiO2 or SnO2.

32. The electrochromic material of claim 1 wherein said electrochromic material is capable of color change upon reduction.

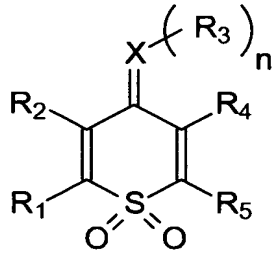
33. The electrochromic material of claim 32 wherein said color change upon reduction is reversible.

34. The electrochromic material of claim 1 wherein said electrochromic material is stable in the reduced and unreduced states.

35. The electrochromic material of claim 1 wherein said electrochromic material is colorless and upon reduction is colored.

36. The electrochromic material of claim 1 which upon reduction exhibits optical absorption between 390 and 750 nm with an extinction coefficient between 5000 M^{-1} cm^{-1} and 25,000 M^{-1} cm^{-1}.

37. An electrochromic device comprising a substrate, at least two electrodes, an electrolyte positioned between said electrodes, an electron donor, and an electrochromic material comprising a substituted-1,1-dioxo-thiopyran of the general structure I:



I

wherein:

X is carbon, nitrogen, oxygen, or sulfur;

n is 0, 1 or 2;

R3 is independently an electron withdrawing group or a substituted or unsubstituted alky or aryl group;

R1 and R5 each independently represent a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group; and

R2 and R4 each independently represent hydrogen, or an electron withdrawing group, or a substituted or unsubstituted alkyl group.

38. The electrochromic device of claim 37 wherein said electrolyte comprises at least one solvent and at least one electrochemically inert salt.

39. The electrochromic device of claim 38 wherein said salt is lithium, sodium and tetraalkylammonium salts or molten salts.

40. The electrochromic device of claim 38 wherein said solvent is transparent and said electrochemically inert salt is soluble therein.

41. The electrochromic device of claim 38 wherein said solvent has a dielectric constant between 10 and 50.

42. The electrochromic device of claim 38 wherein said solvent is selected from the group consisting of acetonitrile, butyronitrile, glutaronitrile, dimethylsulfoxide, dimethylformamide, dimethylacetamide, N-methyloxazolidinone, dimethyl-tetrahydropyrimidinone, 3,3'- oxydipropionitrile, hydroxypropionitrile, dimethylformamide, N- methylpyrrolidone, sulpholane, 3-methylsulpholane, y-butyrolactone and mixtures thereof.

43. The electrochromic device of claim 38 wherein said solvent is acetonitrile, butyronitrile, or γ–butyrolactone.

44. The electrochromic device of claim 38 wherein said electrolyte is in liquid or gel form.

45. The electrochromic device of claim 44 wherein said gel is formed by means of polyelectrolytes, porous solids or nanosize particles.

46. The electrochromic device of claim 44 wherein said gel is formed by means of thickeners selected from the group consisting of polyacrylate, polymethacrylate, polycarbonate or polyurethane.

47. The electrochromic device of claim 37 wherein said electrolyte further comprises at least one UV absorber.

48. The electrochromic device of claim 37 wherein said electrolyte further comprises at least one redox stabilizer.

49. The electrochromic device of claim 37 wherein said electron donor is an organic, inorganic, or organometallic electroactive material that is oxidized reversibly.

50. The electrochromic device of claim 37 wherein said electron donor is at least one member selected from the group consisting of phenothiazines, triarylamines, azines, phenylendiamines, and metallocenes .

51. The electrochromic device of claim 37 wherein said electron donor is a N-substituted phenothiazine, a triarylamines, or a metallocene.

52. The electrochromic device of claim 37 wherein said electron donor is at least one member selected from the group consisting of N-ethylphenothiazine, 5,10-dihydro-dimethylphenazine, N, N-tetramethylphenylenediamine, tri-p-tolylamine, and ferrocene.

53. The electrochromic device of claim 37 wherein said electron donor is located in said electrolyte.

54. The electrochromic device of claim 37 wherein said electron donor is present in at least one of said first electrode or said second electrode.

55. The electrochromic device of claim 37 wherein said electrochromic material and said electron donor are present in said electrochromic layer in the concentration of at least 10^{-4} mol/l.

56. The electrochromic device of claim 37 wherein said electrochromic material and said electron donor are present in said electrochromic layer in the concentration of from 0.001 to 0.5 mol/l.

57. The electrochromic device of claim 37 wherein said electron donor is a Prussian blue material

58. The electrochromic device of claim 37 wherein said electron donor is a polymeric material.

59. The electrochromic device of claim 37 wherein said electron donor is a metal oxide material.

60. The electrochromic device of claim 37 wherein said electron donor is a metal.

61. The electrochromic device of claim 37 further comprising at least one chromophore demonstrating a color change upon oxidation.

62. The electrochromic device of claim 37 wherein said electrochromic material is an insoluble film on said first electrode or said second electrode.

63. The electrochromic device of claim 37 wherein said electrochromic material is chemically bonded to said first electrode or said second electrode.

64. The electrochromic device of claim 37 wherein said electrochromic material is chemisorbed to said first electrode or said second electrode.

65. The electrochromic device of claim 37 wherein said electrochromic material is located in said electrolyte.

66. The electrochromic device of claim 37 wherein said electrochromic material is located in an electrochromic layer.

67. The electrochromic device of claim 66 wherein said electrochromic material is electrochromic layer is in the form of a solution, gel, or solid layer.

68. The electrochromic device of claim 66 wherein said electrochromic layer is a polymer or polymer composite.

69. The electrochromic device of claim 66 wherein said electrochromic layer further comprises at least one UV absorber.

70. The electrochromic device of claim 66 wherein said electrochromic layer further comprises at least one redox stabilizer.

71. The electrochromic device of claim 70 wherein said at least one redox stabilizer is selected from the group consisting of quinones, pyryllium and bipyryllium salts, substituted anthracenes, substituted alkoxybenzenes, and substituted polyhydroxybenzenes.

72. The electrochromic device of claim 70 wherein said at least one redox stabilizer is selected from the group consisting of quinones, substituted alkoxybenzenes, and substituted polyhydroxybenzenes.

73. The electrochromic device of claim 37 wherein said device is an electrochromic window, filter, mirror, or display device.

74. The electrochromic material of claim 37 wherein R3 represents an electron withdrawing group selected from the group consisting of halogen, cyano, COOH, CO_2CH_3, CO_2-alky, $CON(C_2H_5)_2$, SO_2CH_3, SO_2-aryl SO_2CF_3, SO_2-alkyl, PO_3H_2, SO_3H, $B(OH)_2$, or $SO_2N(C_2H_5)_2$].

75. The electrochromic material of claim 37 wherein, when $n > 0$, R3 represents separately or independently substituted or unsubstituted aryl or substituted or unsubstituted alkyl.

76. The electrochromic material of claim 37 wherein said substituted or unsubstituted aryl group is phenyl or naphthyl.

77. The electrochromic material of claim 37 wherein said substituted or unsubstituted heterocyclic group is pyridine, pyrolle, furan, or thienyl.

78. The electrochromic material of claim 37 wherein R1 and R2 or R4 and R5, together with the carbon atoms to which they are attached, form a fused saturated or unsaturated 5 or 6-membered ring.

79. The electrochromic material of claim 37 wherein R2 and R4 each independently represent a hydrogen.

80. The electrochromic material of claim 37 wherein R2 and R4 each independently represent an electron withdrawing group selected from the group consisting of halogen, cyano, COOH, CO_2CH_3, CO_2-alky, $CON(C_2H_5)_2$, SO_2CH_3, SO_2-aryl SO_2CF_3, PO_3H_2, SO_3H, $B(OH)_2$, $SO_2N(C_2H_5)_2$] or a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group.

81. The electrochromic material of claim 37 wherein X represents carbon and the value of n is 2.

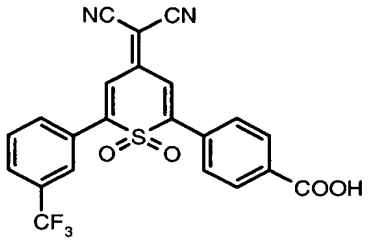
82. The electrochromic material of claim 81 where R3 is halogen, cyano, COOH, CO_2CH_3, CO_2-alky, $CON(C_2H_5)_2$, SO_2CH_3, SO_2-aryl SO_2CF_3, PO_3H_2, SO_3H, $B(OH)_2$, $SO_2N(C_2H_5)_2$].

83. The electrochromic material of claim 81 where R3 is a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group.

84. The electrochromic material of claim 81 where R3 together with the carbon atoms to which they are attached may form a fused saturated or unsaturated 5 or 6-membered ring containing one or more electron withdrawing groups.

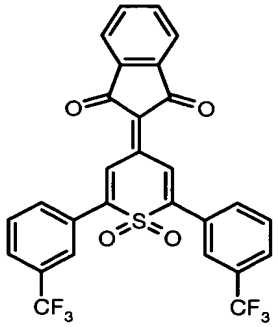
85. The electrochromic material of claim 81 wherein R3 is cyano, alkyester, or indanone.

86. The electrochromic material of claim 81 wherein said electrochromic material is represented by the following structure:



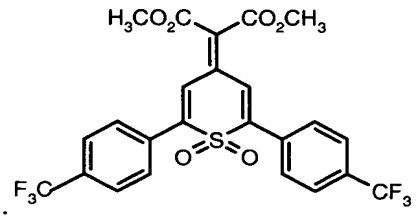
I-7.

87. The electrochromic material of claim 81 wherein said electrochromic material is represented by the following structure:



I-33.

88. The electrochromic material of claim 81 wherein said electrochromic material is represented by the following structure:

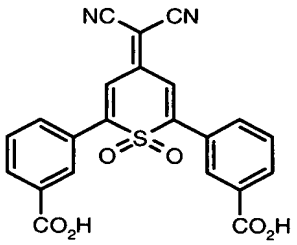


I-44.

89. The electrochromic material of claim 81 that incorporate that incorporate functional groups that facilitate the irreversible chemisorption nanocrystalline metal oxide electrodes.

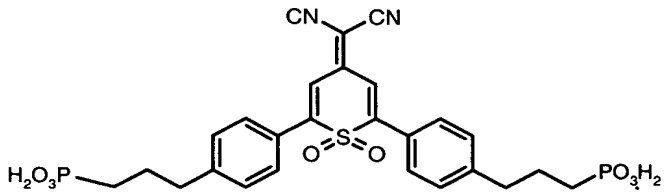
90. The electrochromic material of claim 81 wherein R1 thru R5 together or separately comprise carboxylate, salicylate, or phosphonate groups that facilitate irreversible chemisorption towards metal oxide electrodes.

91. The electrochromic material of claim 81 wherein the electrochromic material is represented by the following structure:



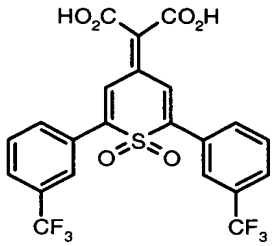
I-14.

92. The electrochromic material of claim 81 wherein the electrochromic material is represented by the following structure:



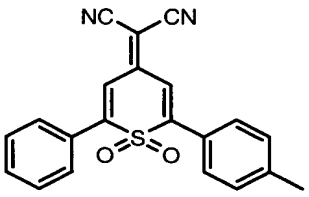
I-67.

93. The electrochromic material of claim 81 wherein the electrochromic material is represented by the following structure:



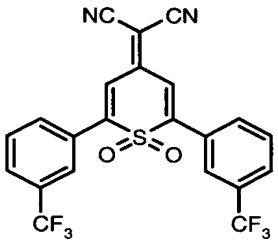
I-46.

94. The electrochromic material of claim 81 wherein said electrochromic material is represented by the formula:



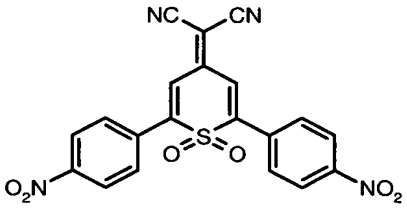
I-2.

95. The electrochromic material of claim 81 wherein said electrochromic material is represented by the formula



I-6.

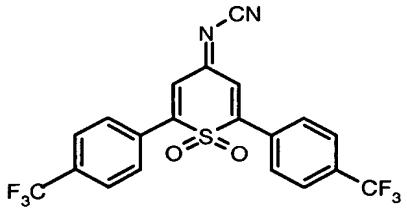
96. The electrochromic material of claim 81 wherein said electrochromic material is represented by the formula



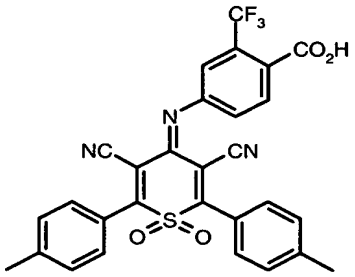
I-8.

97. The electrochromic material of claim 37 wherein X represents nitrogen and n is 1.

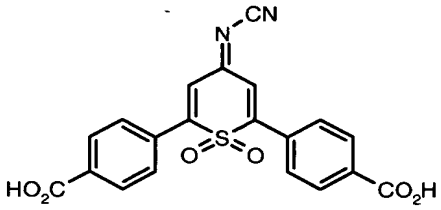
98. The electrochromic material of claim 97 wherein said electrochromic material is at least one member selected from the group consisting of:



I-50,



I-71, or



I-51.

99. The electrochromic material of claim 37 wherein X is oxygen or sulfur, and the value of n is 0.

100. The electrochromic material of claim 37 wherein said electrochromic material has an electrochemical reduction potential of from –1.0 to +0.2 Volts vs SCE.

101. The electrochromic material of claim 37 wherein said electrochromic material has an electrochemical reduction potential of from –0.8 to –0.1 Volts vs SCE.

102. The electrochromic material of claim 37 wherein said electrochromic material has an electrochemical reduction potential of from –0.6 to –0.2 Volts vs SCE.

103. The electrochromic material of claim 37 wherein said electrochromic material comprises electrochromic sulfone structures that have groups for linking to nanocrystalline TiO2 or SnO2.

104. The electrochromic material of claim 37 wherein said electrochromic material is capable of color change upon reduction.

105. The electrochromic material of claim 104 wherein said color change upon reduction is reversible.

106. The electrochromic material of claim 37 wherein said electrochromic material is stable in the reduced and unreduced states.

107. The electrochromic material of claim 37 wherein said electrochromic material is colorless and upon reduction is colored.

108. The electrochromic material of claim 37 which upon reduction exhibits optical absorption between 390 and 750 nm with an extinction coefficient between 5000 M^{-1} cm^{-1} and 25,000 M^{-1} cm^{-1}.

109. The electrochromic device of claim 37 wherein said at least two electrodes comprise a first and second electrode, wherein said first electrode is disposed on said substrate, wherein said substrate is transparent, and where at least one of said first and second electrodes is transparent.

110. The electrochromic device of claim 109 wherein said first electrode is a cathode.

111. The electrochromic device of claim 109 wherein said first electrode is transparent.

112. The electrochromic device of claim 111 wherein said first electrode comprises ITO.

113. The electrochromic device of claim 111 wherein said first electrode comprises fluorine doped tin oxide (FTO), indium tin oxide (ITO), doped zinc oxide.

114. The electrochromic device of claim 113 wherein said first electrode further comprises other metal oxides of indium, titanium, cadmium, gallium-indium, niobium, tin, cerium oxide, zirconium, hafnium and tantalum.

115. The electrochromic device of claim 113 wherein said first electrode further comprises other metal oxides of indium, titanium, or tin.

116. The electrochromic device of claim 109 wherein said first electrode is reflective.

117. The electrochromic device of claim 109 wherein said second electrode comprises an anode.

118. The electrochromic device of claim 109 wherein said second electrode is transparent.

119. The electrochromic device of claim 118 wherein said second electrode comprises ITO.

120. The electrochromic device of claim 118 wherein said second electrode comprises fluorine doped tin oxide (FTO), indium tin oxide (ITO), doped zinc oxide.

121. The electrochromic device of claim 120 wherein said second electrode further comprises other metal oxides of indium, titanium, cadmium, gallium-indium, niobium, tin, cerium oxide, zirconium, hafnium and tantalum.

122. The electrochromic device of claim 120 wherein said second electrode further comprises metal oxides of indium, titanium, or tin.

123. The electrochromic device of claim 109 wherein said second electrode is reflective.

124. The electrochromic device of claim 37 wherein said electrochromic material is located in an electrochromic layer.

125. The electrochromic device of claim 124 wherein said electrochromic material is electrochromic layer is in the form of a solution, gel, or solid layer.

126. The electrochromic device of claim 124 wherein said electrochromic layer is a polymer or polymer composite.

127. The electrochromic device of claim 124 wherein said electrochromic layer is an insoluble film on said first electrode or said second electrode.

128. The electrochromic device of claim 124 wherein said electrochromic layer is chemically bonded to said first electrode or said second electrode.

129. The electrochromic device of claim 124 wherein said electrochromic layer is chemisorbed to said first electrode or said second electrode.

130. The electrochromic device of claim 109 further comprising at least one reflective nanoporous-nanocrystalline semiconducting film that is intermediate to said first electrode or said second electrode.

131. The electrochromic device of claim 130 wherein said electrochromophore is chemisorbed to said at least one of said nanoporous-nanocrystalline semiconducting films.

132. The electrochromic device of claim 130 wherein said nanocrystalline semiconducting film is a metal oxide.

133. The electrochromic device of claim 132 wherein said metal oxide is any suitable metal selected from the group consisting of titanium, zirconium, hafnium, chromium, molybdenum, tungsten, vanadium, niobium, tantalum, silver, zinc, strontium, iron (Fe^{2+} or Fe^{3+}), nickel or a mixed metal oxide thereof.

134. The electrochromic device of claim 132 wherein said metal oxide is any suitable metal selected from titanium, molybdenum, or tungsten.

135. The electrochromic device of claim 130 wherein said nanocrystalline semiconducting film is TiO_2 , WO_3 , MoO_3 , ZnO, SnO_2 and SnO_2 doped with Sb.

136. The electrochromic device of claim 130 wherein said nanocrystalline semiconducting film is TiO_2 , SnO_2 and SnO_2 doped with Sb.

137. The electrochromic device of claim 130 wherein said at least one nanocrystalline semiconducting film is independently deposited on said first electrode and said second electrode.